

THE
PURIFICATION OF DRINKING WATER

BY
THE USE OF OZONE

BY
GEORGE A. SOPER, B.S., M.A.

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY, IN THE FACULTY
OF PURE SCIENCE, COLUMBIA UNIVERSITY.

NEW YORK
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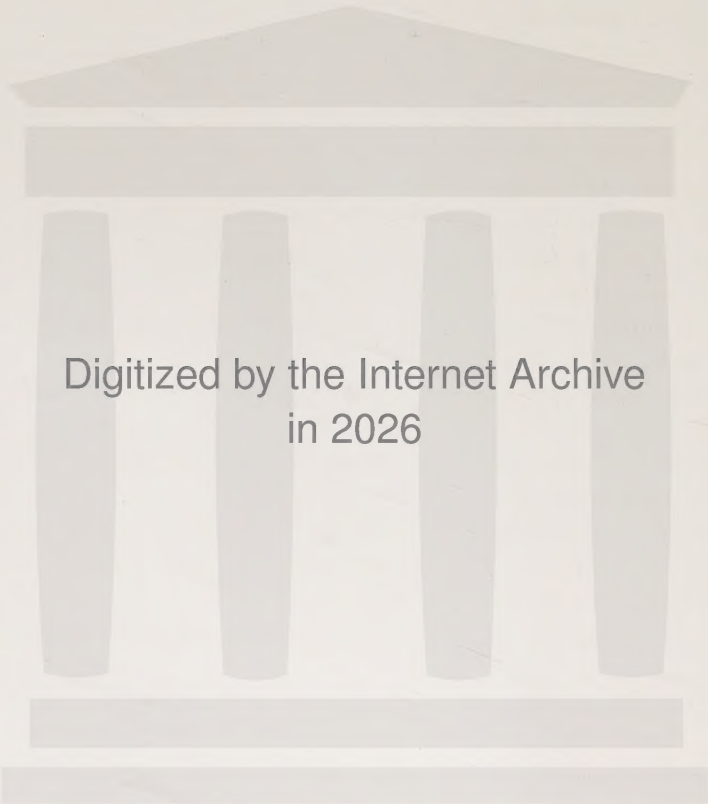
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OCCURRENCE, PROPERTIES AND ESTIMATION OF OZONE.

It is a matter of common experience that where electric sparking takes place in the presence of air there is formed a characteristic and unpleasant odor. This was observed by Marum in 1785, and in 1840 Schönbein began to publish notable memoirs upon the subject, ascribing the odor to the presence of a new form of matter which he named ozone. Schönbein found that ozone could be produced by the electrolysis of dilute sulphuric acid and by the slow oxidation of phosphorus. In 1845 Marignac and De la Rive found that pure oxygen could be completely converted into ozone, and Andrews, Soret, Brodie and Tait contributed facts which demonstrate that ozone from all sources is identical, and that it is an allotropic form of oxygen, with the formula O_3 .

Ozone has been made in quantity by the electrolysis of acidulated water, by the slow oxidation of phosphorus and by the discharge of electric currents. The most approved method is by the use of the silent discharge of electricity, which may be defined as the transference without sparking of a current of high potential and small volume across a space between two electrodes. Under properly regulated conditions, the silent discharge is accompanied by the phenomenon of a distinctly violet-colored flame. In the presence of the flame pure oxygen, or oxygen contained in the atmosphere, is in part converted into ozone; about 15% of the oxygen being altered, according to Professor Armstrong. Practical experience with large ozonizers indicates this figure to be too high, and that not more than 1% of the oxygen of the air can be safely counted upon. From the fact that ozone is supposed to be a constituent of the atmosphere, possessing

germicidal properties, attention has been directed to means for its formation in simple apparatus for the disinfection of hospital wards, etc. The reaction due to the slow oxidation of phosphorus has generally formed the basis of such devices, but the beneficial effects of treating foul air with manufactured ozone have not received scientific confirmation. The occurrence of ozone in the air is still a matter of dispute, according to Professor Ramsay in his "Gases of the Atmosphere."

The chemical properties and reactions of ozone indicate that its general action is that of a strong oxidizer. It appears to have no effect on dry metallic gold, platinum, copper, aluminum or silver, although in the presence of moisture its characteristic test is the oxidation of the last-named element. Ozone is capable of throwing iodine out of combination with potassium, in potassium iodide, with the formation of caustic potash; a reaction which has given rise to a method for the quantitative estimation of O_3 . Ozone oxidizes ammonia and nitrites to nitric acid, attacks India rubber and is a strong bleaching agent, especially in the presence of chlorine, destroying vegetable coloring matters, and I find that foul odors of organic origin are removed by it. The presence of ozone is usually determined by paper saturated with KI and starch, but Professor Shenstone points out that such tests are conclusive only in the absence of chlorine and oxides of nitrogen. Houzeau used paper treated with faintly acid litmus and potassium iodide. When exposed to ozone, the litmus turned blue by the formation of KOH. Traces of nitrogen compounds and H_2O_2 will not affect the result. The method of estimating ozone, which I have adopted in connection with my apparatus for producing a continuous current of ozone, depends upon the dissociation of potassium iodide. One hundred c.c. of a 5% solution of KI, free from iodate, is placed so as to catch the continuous stream of ozonized air to be examined. The ozone is bubbled through the potassium iodide which quickly absorbs it, iodine being liberated at the same time. In order to take up the KOH formed, a constant stream of small bubbles of CO_2 is passed through the KI solution. After a sufficient quan-

tity of air has passed through the apparatus it is disconnected, and the iodine solution titrated with a fresh hyphosulphite of soda solution of such strength that 1 c.c. corresponds to 0.25 mg. of oxygen. Starch solution is used as an indicator. The method is taken from Mohr's "Titrimethode," sixth edition, revised by Classen.

APPLICATIONS OF OZONE.

Notwithstanding the strongly oxidizing properties of ozone and the abundant supply of oxygen from which it may be produced, no successful attempt seems to have been made until recent years to manufacture it upon a commercial scale. To-day there is but one economical method for its production, and its application in the various chemical processes to which, from speculative reasons, it might seem adapted, is extremely limited. Ozone is rather regarded as a curiosity of chemistry than as a reliable oxidizing agent, and the U. S. patents for making it indicate that its supposed disinfecting properties constitute its chief value. Recently, however, the oxidizing properties of ozone have attracted attention, and companies have been formed to manufacture ozone and apply it to various industrial purposes. Among such companies may be mentioned the Commercial Ozone Syndicate of Great Britain, an account of whose operations I have recently had the honor to review before the Chemical Society of Columbia University. Among the industries in which ozone is claimed to be successfully employed may be mentioned the ageing of spirits and wines, the preserving of coffee, the seasoning of wood for pianos, the purification of oils and the bleaching of linens and other fabrics. Within a few years ozone has been used to sterilize water. The process has been developed by Baron Henry Tindal, of Amsterdam, Holland. Mr. Tindal's plants and the experiments which led up to them, represent the only attempts ever made, so far as I am aware, to sterilize large volumes of water except by the familiar methods of filtration and evaporation. I have visited the Tindal plants at Blankenberg, on the Belgian coast, and Paris, and have been able to collect first hand many of the facts here presented relating to the process.

THE TINDAL EXPERIMENTS.

It has been claimed by Mr. Tindal that the purification of water by ozone is a natural process. Wherever water lies exposed to the influence of the air and sunlight there is a purifying effect which he considers must, in part at least, be attributed to the agency of ozone. The idea of improving the quality of drinking water by this supposed constituent of the atmosphere is therefore not novel. The novelty of the Tindal process lies in the arrangement of artificial conditions whereby the beneficial effects ascribed to ozone may be produced in a thorough and reliable manner.

The first experiments with the Tindal system were undertaken at Oudshoorn, near Leyden, Holland, in 1893. It had been shown by Frölich, during the course of investigations made by him for the engineering and contracting firm of Siemens & Halske of Berlin, that ozone produced by subjecting a current of atmospheric air to the action of a silent discharge of electricity possesses the important property of destroying microorganisms, and that its action is most effective in the presence of moisture. In this respect Frölich's research confirmed those of Kowalowski and Krukowitsch of Russia and Christmas of Paris, who investigated the germicidal action of ozone and whose results appeared at about the same time. Frölich's investigations, however, are believed to furnish the first practical suggestions of the value of a satisfactory system of ozonizing water. In a paper contained in *Electrotechnische Zeitschrift*, No. 26, 1891, and in *Gesundheits-Ingenieur*, XIV., 543, 1891, Frölich states that ozonization probably sterilizes water, converts ammonia into nitrites and nitrates, precipitates iron as hydroxide and destroys sulphuretted hydrogen; he further suggests the important fact that ozonization must follow, and not precede, filtration. Frölich's efforts were especially directed to the development of an effective and economical apparatus for the production of ozone which might be used in various industries, and the hygienic applications of ozone were not conclusively worked out by him.

The sterilizing action of ozone was left for Ohlmüller to in-

investigate officially for the Imperial Board of Health of Germany. His report is entitled "Über die Einwirkung des Ozones auf Bakterien," and is contained in *Arbeiten aus dem Kaiserlichen Gesundheitsampt*, T. VIII., Part I. The plant with which Ohlmüller and his three associates experimented, was situated at Berlin, and consisted of a 1 h. p. gas engine, a 65-volt-8-ampère dynamo and an induction apparatus. A Siemens ozonizer was used, and the air was measured with a gas meter. With this outfit Ohlmüller produced 3 milligrams of ozone per second. He operated upon water from the Spree, and distilled water to which known amounts of impurities were added. Spree water was sterilized in ten minutes with 83.6 mgs. ozone, sewage was not sterilized in an hour with 156.3 mgs. ozone, but distilled water to which bacteria in great numbers had been added, was sterilized most easily. Anthrax bacilli to the number of 3,717,000 per c.c. in distilled water were killed in ten minutes, with 89.9 mgs. ozone. In another case, 57,000 anthrax bacilli were destroyed in ten minutes with 58 mgs. ozone. In two minutes, 12,247,000 typhoid bacilli were killed with 19.5 mgs. ozone; and in still another case, in two minutes, 2,791,000 cholera bacilli were destroyed with 16.5 mgs. ozone. Ohlmüller's conclusion was that where waters are not too contaminated with solid organic impurities, ozone exerts a destructive action upon bacteria.

The Tindal plant at Oudshoorn was the object of an investigation by Professor Van Ermengem, of the University of Ghent, whose research was carried on at the request of the Government, and whose report was tendered to the Minister of Agriculture and Industries, of Belgium, July 30, 1895. An abstract of the paper is to be found in the *Annales de l'Institut Pasteur*, Vol. IX., p. 673. The water used in the Oudshoorn experiments was drawn from the Old Rhine, which at this point is little more than a drain for the polders and factories and towns in the vicinity. The quality of the water was variable, with much organic matter, a disagreeable odor and a distinct brown color. In order to remove suspended matter which would interfere with the process the water was first stored in a small cistern and then filtered at

the rate of two and one-half million gallons per acre per day through a slow filter. The water was then ozonized by having a current of cold, dry air, which had been subjected to the silent discharge of electricity, bubbled through it. The quality of the water of the Old Rhine, at Oudshoorn at each stage of its purification may be observed in Table I. of the appended tables. The results of many analyses of the water before and after ozonization are conveniently summarized in Table II. In order to comprehend the latter table fully, it should be understood that bacteria of known species were occasionally planted in known numbers in the untreated water, and that the numbers of such bacteria found in the effluent were compared with them. Ptomains, toxalbumins, and other poisonous products of bacterial activity were also added to the water on several occasions, with the result that their presence was never discovered in the water after ozonization.

The apparatus employed at Oudshoorn for the production of ozone was, like the apparatus of Frölich and Ohlmüller, adapted to the silent discharge of electricity. In the presence of the silent discharge, pure oxygen, or the oxygen contained in atmospheric air, is in part converted into ozone, while in the spark discharge of electricity compounds of oxygen and nitrogen are believed to be formed also. In the Siemens and Halske experiments, dielectrics had been used between the electrodes, the purpose in interposing such nonconducting surfaces having been to regulate the current so that the discharge might be uniform and constant. With sufficient potential in the electrodes, currents of opposite sign are induced by dielectrics and the discharge takes place, in most forms of ozonizers, between walls of glass, the electrode consisting of sheets of metal foil. By passing a current of air through the space formed between the dielectrics, a continuous supply of ozone may be produced. At first, a large Siemens tube with celluloid dielectrics was employed by Mr. Tindal, but it was impossible to insure satisfactory working with it at very high voltages. Frölich and Ohlmüller found that there was danger of rupturing glass dielectrics with electrical pressures above 4,000 volts.

Credit is due to Schneller, an electrician in the employ of Mr. Tindal, for devising means whereby solid dielectrics may be dispensed with. By substituting a liquid cell of known resistance for the solid dielectrics usually employed in ozonizers, Schneller opened the way for currents of higher electro-motive force than had thus far been experimented with, and the result is claimed to have been an increased yield of ozone. The cell consisted of a thin glass tube 60 cm. long, filled with a mixture of glycerine and alcohol and fitted at each end with wire connections. It was suspended directly above the ozonizer, to whose positive electrode it was electrically attached. The ozonizer consisted of a positive electrode, composed of a series of pieces of thin platinum foil, inclosed in a metallic box, from which it was separated at all points by a space of 2-3 millimeters. The box was in electrical communication with the earth and thus served as a negative electrode. The electrical discharge took place between the sheets of foil and the metallic box. Air forced through this apparatus was ozonized. In order to supply the high potential desired, Mr. Schneller designed two step-up transformers which were operated in series, taking current from an alternating current dynamo giving 100 volts and 14 amperes, and transforming it to 50,000 volts. It was found advantageous to subject the air to several ozonizations. This was done by forcing it through a battery of ozonizers. The air, however, was first freed of dust by filtration through cotton, then dried by passing through desiccators containing calcium chloride and sulphuric acid, and finally refrigerated by the aid of an ice-making machine. The air was further chilled on its passage between the ozonizers.

On leaving the ozonizers the ozonized air was forced by a pump to the sterilizers. Two models of sterilizer were tried; in one a rain of water met an atmosphere of ozone and in the other the ozone was bubbled through a column of water. The bubbling system appears to have been the more economical, and it is the one subsequently preferred by Mr. Tindal.

Unfortunately Professor Van Ermengem's report does not deal with the economic questions involved in Mr. Tindal's plant at

Oudshoorn. It concerns itself only with the qualitative efficiency of ozonization.

The first public demonstration of the Tindal system of purifying water by ozone was made at Paris, at the Hygienic Exhibition on the Champ de Mars, in 1896. The plant was tested as to its capacity for stérilizing the water of the Seine, by Dr. Marmier and Dr. Repin of the Pasteur Institute. A memoir by Dr. Repin entitled "Stérilization de l'eau par l'ozone," appears in *Rev. Gen. des Sciences*, Vol. VII., p. 596. The line of investigation was similar to that pursued by Van Ermengem at Oudshoorn, and the qualitative results were much the same. The electric current used for the ozonizers was taken from an electric light alternating current machine of 120 volts, 10 ampères, which was transformed to 50,000 volts for the silent discharge. The ozonizers consisted of a series of glass-lined boxes, 25 cm. $\times$ 35 cm. $\times$ 60 cm. Supported in each box, and insulated from it, was a rectangular package of platinum foil sheets. Opposite the edges of the platinum, and upon the glass, were fastened sheets of gold. Glycerine-and-alcohol resistance cells, similar to those already described, were suspended above the boxes. The silent discharge took place between the platinum and the gold. All other apparatus was substantially such as had been used at Oudshoorn. The sterilizers brought about a contact between the ozone and water by bubbling. The water was filtered through sand before ozonization. The effect of the process was satisfactory, and in Table III may be seen the results of three chemical analyses of Seine water before and after ozonization. Dr. Repin says that where water does not contain more organic matter in solution than is represented by 0.004 gram permanganate per liter, 5 cubic meters may be purified by the expenditure of 600 watts.

The third installation of the Tindal system was constructed at the Brussels International Exhibition in 1897, where it was made the subject of investigation by Professor Van Ermengem and Professor Leon Gerard, of the University of Brussels. The research was made in order to secure information which would

assist in improving the sanitary condition of towns on the Belgian coast whose water supplies are well known to be frequently inferior in quality. At first the water treated at Brussels was that of the general city supply, which is obtained from infiltration galleries. Later, with smaller apparatus, samples of 200–250 liters collected elsewhere, were ozonized. Mr. Tindal's apparatus at the Brussels Exhibition had a capacity of 432 cubic meters of treated water per day. The plant was essentially like those already described. The consumption of energy per gram of ozone produced, was 244–252 watts. The electrical energy per cubic meter of water sterilized, was 75–95 watts. The cost of ozonizing water containing 0.100 gram organic matter per liter was less than one centime per cubic meter. The experiments at Brussels confirmed the favorable reports already made upon the Tindal system and demonstrated that some highly polluted waters may be satisfactorily purified upon a commercial scale when they do not contain organic matter in suspension. The effect of ozonizing Brussels water may be seen in Table IV. Experiments with water from the Ostende supply, from the canal of Plaschendaël and the canal of Bruges, two possible sources of water supply, are indicated in Table V. Interesting details concerning the energy absorbed in producing ozone by the Tindal process may be seen in Table VI.

There are in Europe at the present date two municipal sterilization plants operated upon the principles just outlined. Both were constructed by private enterprise subject to the examination of competent scientific experts, and upon the demonstration of their capacity for purifying the water supplied to them, they were accepted and paid for by the municipalities. The first plant referred to is situated at Blankenberg, on the Belgian coast. It receives canal water filtered by the Howatson process, which in America would be considered a crude system of mechanical filtration.

The second municipal plant is situated at Joinville le Pont, in the environs of Paris, for the sterilization of Marne water, after filtration through slow filters. Details of the cost of sterilizing this water are as follows:

Energy required for ozonizer,	3.0 h. p.
“ “ “ air pump,	1.5 “
“ “ “ water pump,	12.0 “
Total energy,	16.5 h. p.
Cost per day, at 2 cts. per h. p. per hr., . . .	\$7.90
Other daily expenses are :	
Salaries of three men at \$200 per month,	\$6.66
Interest charge of $3\frac{1}{2}$ per cent. upon \$20,000 (cost of plant),	1.94
Interest charge of 4 per cent. upon \$20,000 (to cover depreciation),	2.22
Total salaries, etc.,	10.82
Cost of energy,	7.90

Capacity of plant, 3,170,000 gals. per 24 hours. Operating expense, \$18.72 per day.

This is at the rate of \$5.90 per million gallons.

MY LABORATORY EXPERIMENTS.

The apparatus employed by me for the production of ozone and its application to the purification of water, consisted of a motor-circuit-breaker producing 4,000 breaks per minute, an 18-inch Ruhmkorff coil, a Siemens tube, a gas meter, and some glass chambers in which the ozone and water were brought into contact. Current was taken from the electric light installation of the University grounds, and the water operated upon was usually the Croton supply previously filtered through “Continental” rapid filters, containing charcoal and sand. Most of the electric current was cut out by a resistance frame and shunt, and only a small portion was allowed to enter the Ruhmkorff coil. The spark obtained from the latter under these conditions was 5 inches long. From the outset of the experiment considerable difficulty was found in making air-tight connections which would withstand the action of ozone. No form of rubber would remain exposed to the ozonized air more than a few minutes without

becoming pitted and shredded. A sealing mixture of beeswax, rosin and Venice turpentine, heated to make an even cement, proved nearly worthless because of difficulties connected with its application. Cork was not found to be attacked by ozone, but it was not possible to secure tight joints between small glass tubes with any quality of cork at my disposal. Finally, thin silk ribbon, painted with gum shellac, was wound about the joints and then whipped with heavy silk thread. After coating such joints with shellac varnish they were usually found to be tight. Such joints were not flexible, an objection which I have not been able to overcome and which has frequently hampered a convenient arrangement of the apparatus.

The ozonizer placed at my disposal was an old Siemens tube, 18 inches long and $1\frac{3}{4}$ inches outside diameter. One end of the tube tapered to a $\frac{3}{8}$ -inch tube, 2 inches in length, and at the other end there was a tubulation of the same diameter. Within the large tube, and separated from it by pieces of cork, was a second tube $1\frac{1}{8}$ inches in diameter which was closed and fitted into the first by means of a tight stopper. The outside of the large tube and the inside of the small tube were covered with tin foil and suitably arranged with separate wire connections. Eventually the inner foil was replaced by tin filings. The whole rested on a wooden stand, in a horizontal position. Air was passed into the annular space between the glass walls of the two tubes, through the side tubulation and ozonized by contact with the silent discharge of electricity which took place when the wire connections of the ozonizer were joined to the poles of the Ruhmkorff coil. It was soon found in practice that the ozonizer thus operated became very hot, and that some means for cooling the air and reducing the temperature of the ozonizer were needed. Various plans and several ozonizers were tried, with the result that an ozonizer of the following description was adopted. A $\frac{1}{4}$ -inch block tin tube was fastened in the form of a worm about the inner walls of a cedar bucket 19 inches high and 13 inches in diameter. The lower end of the worm passed through a permanent false bottom, downward at the pe-

riphery and upward at the center. Here it was joined to the old Siemens tube, whose pointed end was hermetically sealed to the block tin pipe. The upper end of the Siemens tube projected slightly above the top of the bucket so that the side of the tubulation was conveniently connected to tubes supplying the sterilizers. The bucket was then filled with water. As desired, a freezing mixture or a current of cold water was maintained in the bucket, with the result that the air feed was kept at a low temperature and the ozonizer was prevented from heating. It is believed that this arrangement is novel. The air to be ozonized was first filtered through cotton to remove dust particles, then measured through a gas meter, passed through a scrubber of pumice stone and potassium hydrate to remove carbon dioxide and finally through a scrubber of pumice stone and sulphuric acid to dry it, whence it proceeded to the ozonizer. The air was kept in motion by an aspirator attached to the sterilizer, which produced a negative pressure in the whole apparatus.

The water experimented with was at first held in eight-gallon tincture bottles, and ozonization was effected by passing bubbles of ozonized air through 6 gallons of water thus contained. Difficulties with temporary connections, however, made it impracticable to continue the use of bottles. Another plan of ozonization consisted in atomizing a small stream of water with a current of ozone, and for this purpose the bottles described were turned upside down and atomizing devices attached through the stoppers. By properly regulating the supply of ozonized air and water, the bottles could be filled with a fine spray or heavy rain. This collected upon the sides of the bottles, ran down and was carried off by an exhaust. Atomization made it necessary to provide a second bottle to catch the product, and with such an arrangement it was difficult to determine the interval of contact between the water and ozone. A cylinder of stout glass, 25 inches long and 6 inches in diameter, abruptly tapering at the ends and fitted with stoppers, was then selected to replace the bottles, because of the facility with which water and ozone connections could be made at its top and bottom. With

this form of sterilizer arranged as an atomizer several interesting tests were made.

A dark-brown infusion of tobacco leaves was prepared and filtered. Of this filtered infusion enough was added to a quantity of distilled water to produce a color corresponding to 6 of Hazen's platinum-cobalt standard scale. After atomization the color was reduced to 3 of the standard. A second atomization reduced the color to 1. The total reduction of color was, therefore, 83.3 %. Subsequent tests gave results similar to the foregoing, but it was found, when Croton water was substituted for distilled water, that the product became opalescent. In all cases the last traces of color were slow to disappear.

With the idea of testing the effect of ozone upon disagreeable odors, such as occasionally give rise to complaints against water supplies, the following series of experiments were arranged. Nearly equal weights of herring, onion, geranium leaves, cinnamon and putrid beef were soaked in separate bottles of distilled water for 48 hours, and then filtered off. The odors absorbed by the water were very pronounced. Each sample was then atomized with ozonized air and the odor again noted. The reduction was considerable in each case. After a second treatment there was scarcely any odor perceptible in the herring, beef and onion waters. The geranium and cinnamon samples smelt slightly of ozone, but whether they had absorbed enough ozone to make the odor noticeable or whether it was due to a mechanical admixture of ozonized air was not apparent. Upon aerating the water the smell of ozone disappeared.

In the color and odor experiments it was observed that a definite time interval was required in order to insure a proper reaction with the ozone and that no matter how intimate the contact, purification was not instantaneous. Supposing it might be more important to provide for a long exposure than a particularly intimate one, apparatus was devised whereby a fairly intimate contact could be maintained for a longer period. The plan had the further advantage of requiring less power to keep the water and air in circulation. Into the top of the cylinder described was set

a small glass aspirator. Water to be treated was furnished to the aspirator under suitable pressure, and as it passed through the aspirator it entrained ozone. Ozone and water then passed into the cylinder, where the water fell upon a plate and spattered to the sides. It was found that the use of the aspirator required too much water for the quantity of ozonized air entrained.

The next form of sterilizer used consisted of a series of seven cylinders like the one already described, arranged in a row in a permanent wooden case. It had been found that large bottles were unserviceable from the difficulty experienced in cleaning them. To clean, fill or empty them, it was necessary that they should be free to move, or arranged with a system of syphons and supply pipes. With permanent inflexible joints upon the ozonized air pipe, a large movable sterilizer was impracticable, while the small size of the stoppers necessary for air-tight joints did not permit of large pipes on many of them. The cylinders could be operated at both ends. Their capacity was large and they offered facilities for a large range of adjustment of piping. The battery of cylinders was first connected at the bottoms by block tin piping, $\frac{1}{8}$ in. in diameter, in such a way that ozonized air and water which was made to enter the first, would pass in succession through each cylinder. The outlet end of each tube was reduced, to give force to the water leaving it. When the system was in operation, a continuous spray was formed through all the cylinders. Experiments were made with various coloring agents, in this apparatus. Very dark infusions of dried leaves, darker than the color of any water which would be likely to be considered fit to drink, were completely bleached by this system. Solutions of red and blue litmus, indigo and alizarine were also decolorized. It was evident that such thorough and protracted contact would probably not be required for any drinking water to be met with in practice, and there were practical difficulties in the way of using the battery as permanent atomizers. Air pressures were difficult to manage in so many large chambers, and the tin tubes showed a tendency to become clogged with disengaged particles from the paraffin with which the rubber stoppers had been

coated. Cork stoppers had not been found tight, even when boiled in paraffin and coated on the outside with wax-rosin cement. Rubber stoppers boiled in paraffin lost their coating by scaling. The stoppers finally used were made of rubber, scraped to remove adhering matters, and varnished with shellac.

The second form of adjustment of the cylinders was as follows: cylinders Nos. 1 and 2 were connected at their bases so that either could be filled or emptied readily, and a free communication opened between them. From the top of cylinder No. 1 to the bottom of cylinder No. 2, a glass tube was fitted. Further, there were tubes for the ozonized air to enter at the bottom of No. 1, and escape at the top of No. 2, where an aspirator was connected. Between the ozonizer and sterilizers was a series of cocks for regulating the quantity of water, ozone and air which it might be desired to draw into the cylinders. This was the final adjustment of the apparatus. The water to be treated is ordinarily run into sterilizers Nos. 1 and 2, until they are two-thirds full. Cylinder No. 3 is filled at the same time and kept closed in order that its contents may serve as a comparison. The other cylinders are permanently out of service in this adjustment. When the preparations indicated have been made, the electricity is turned on and the aspirator opened. Ozonized air bubbles up through the first and second cylinders until their contents are sufficiently purified. In operating the apparatus with a continuous supply of water, the water is admitted at the bottom of No. 1 and withdrawn at the bottom of No. 2. If a case should arise in which further ozonization was desired, other cylinders could be connected to Nos. 1 and 2, in the manner described for Nos. 1 and 2.

My chemical analyses of Croton water before and after treatment by this system have shown a notable degree of purification. Nitrites disappear, albuminoid ammonia and free ammonia are oxidized, and a considerable reduction in color effected. As previously indicated, odors are destroyed by ozone and the water after treatment is attractive to the sight and taste.

It was found that the sterilizing power of ozone is a difficult

question to investigate in a laboratory not especially suited to the refinements of bacteriological technique. To establish the fact of absolute sterility requires methods and apparatus quite different from that ordinarily met with. The sampling should be done in a manner to exclude the possibility of contamination by air and similar influences, a detail but imperfectly observed in much bacteriological work. That water samples sown and plated in the ordinary way frequently develop colonies from the air, has been shown by Van Ermengem, in *Annales de l'Institut Pasteur*, Vol. IX. Many microorganisms, especially those of a pathogenic nature, will not develop in gelatin at ordinary temperatures, but require special media such as agar, milk, potato, bouillon, kept at or near blood heat for a considerable period of time. The methods used by me were not of this refined character and sterility was not proved to exist in any samples examined. The samples were collected in sterilized glass bottles and sown immediately. One cubic centimeter of water was mixed with ten c.c. of beef gelatin of such reaction that 1,000 c.c. required 15 c.c. normal NaOH to make it neutral to phenolphthalein. The mixture was poured upon Petri dishes and allowed 48 hours to develop at room temperature before counting. My bacteriological results show a decided reduction in the number of bacteria after ozonization, which agrees with the partial removal of color and organic matter already alluded to.

CONCLUSIONS.

A consideration of the facts here presented leads to the conclusion that drinking water can be sterilized, and that unpleasant colors and odors arising from organic impurities can be removed by ozone. It remains to be shown what class of waters are best suited to the treatment and the conditions under which ozonization may be successfully carried on.

The action of ozone in the artificial purification of water is a chemical one. It is unlike other methods in that no mechanical or biological actions contribute to the result. By ozonization, chemically active oxygen is brought into contact with oxidizable

impurities, which thereupon suffer transformation into more stable compounds. No suspended matters are removed or destroyed, except the bacteria, and in this respect the ozone treatment differs from the more familiar methods of filtration and sedimentation. Consequently, the class of waters susceptible of purification by ozone are generally free from organic particles. Such, for example, are clear, colored or foul-smelling surface or ground waters and the effluents of improperly acting filters.

The claims made for the ozone treatment of water are distinct and its functions are as clearly defined as are those of filtration and sedimentation. Ozonization aims to eliminate bacteria from water and to destroy unpleasant colors and odors of vegetable origin. From a consideration of all obtainable data I am led to the conclusion that this result is possible.

The impurities in drinking water may be roughly grouped into those matters which cause turbidity and those which cause disease, and it may be stated that settling basins and filters are usually employed to remove the one and the other of these impurities. Leaving aside the question of the action of settling basins, since their functions are quite distinct and generally understood to be confined to the removal of the coarser impurities, it will be interesting to consider for a moment the manner in which filters commonly act in the purification of drinking water.

Two types of filters are known to the art and may be designated "rapid" or "slow" according to the speed with which they are designed to operate. In each case the filtering medium consists of a sand bed, but they are radically different in their proportions and method of action. The older type, or slow filters, depend upon a layer of vegetable matter which forms upon their surfaces, to strain out bacteria and such other impurities as may be associated with them. Their action is imperfect without the vegetable layer and their efficiency depends upon its proper formation and integrity. The rapid type of filters purify water at a rate which is at least forty times that suitable for slow filters, and depends upon some kind of chemical coagulant which collects together in flocculent masses the minute particles of matter which it is desired to remove.

Both types of filters, under favorable conditions may effect a certain amount of oxidation of organic matters dissolved in the water, but their chief value depends upon their capacity as strainers. Filters frequently remove a considerable percentage of bacteria, and when 99 per cent. of the bacteria are known to be removed, the filtered water is commonly believed to be exceptionally pure. Such an assumption may, however, be misleading, since the mere percentage of removal gives no evidence of the number or kind of bacteria that escape. Thus, in cases where the original number of bacteria exceed 20,000 per c.c., the number left after a removal of 99 per cent. will exceed 200 per c.c., or in a glass of water, 40,000. If the percentage of removal is 98 instead of 99, there will be twice as many bacteria in the filtered water.

It would seem that the principles of filtration are commonly enough understood to make it possible for almost any one to construct a water filter, but the elements upon which the permanent usefulness of filters depends have long been the subject of investigation in this country and Europe, and their proper design demands the experience and skill of experts. The operation of slow and rapid filters requires intelligent and watchful care if high removals of bacteria are required, and the delicate operations of applying chemicals, cleaning the beds and regulating the flow assume an aspect of great importance when viewed in the light of their influence upon the filtered water.

The function of ozonization puts at a discount the possible ignorance and carelessness of filter keepers and places the responsibility for pure water in the hands of electricians and engineers whose familiarity with machinery makes them competent to manage the mechanical details of the process. There is no cleaning of apparatus in the ordinary case, no stopping and little regulating to be done. The proper dose of ozone is known by the presence or absence of its peculiar odor when observed at the top of the water column.

Ozonization is in no sense a straining process and from its nature could not be expected to sterilize waters containing large

quantities of matter in suspension. Consequently for the proper treatment of water by ozone, filtration is in most cases indispensable, but the kind of filtration which may be termed a simple straining, is as effective as any other in preparing the water for ozonization.

Of special importance is the completeness with which ozone destroys unpleasant odors in water. When filtered water or ground water is exposed to heat and light, forms of vegetation are apt to grow and cause trouble. Films or cloudy masses of algae appear under such circumstances, and frequently cause fishy, pungent, aromatic or disgusting tastes and odors in the water. It seems certain that ozonization of such a water, previously filtered to remove the objectionable organisms, etc., would restore it to its former acceptable condition.

Household installations for sterilizing water by ozone are not practicable, inasmuch as the apparatus required would be too expensive on so small a scale.

For laboratory experiments I would recommend such apparatus as that elsewhere described as the final adjustment of the apparatus used in my experiments. The sterilizers can be used on the continuous or intermittent plan and the period of contact between water and ozone may be varied between desirable limits for all waters likely to demand sterilization. It is believed that the design of the ozonizer, sterilizer and regulating devices is original, and that the removal of such dark colors and strong odors from drinking waters have not before been accomplished. In selecting the impurities for experiment special reference was had to the natural colors of deep stained waters and to the peculiar effects due to growths of algae which have become recognized as the cause of disagreeable odors and tastes.

Desirable improvements upon the apparatus include a dynamo supplying an alternating current, with transformers to raise the voltage and means to force the current of ozonized air through the sterilizers without the necessity of an exhaust. Such facilities were, however, not available for my research, and in their absence the foregoing devices proved fairly satisfactory.

I desire to make suitable acknowledgment to Professor C. F. Chandler, for the privilege of using his private laboratory and lecture apparatus for the purposes of my experiments and for his kindness in furnishing me with literature, sometimes taken from his personal library. Messrs. Laudy, Lovejoy, Freedman and Professor Hallock have given me assistance in the work.

Previous publications by G. A. Soper include a *Report on the Efficiency and Betterment of the Hudson City Filter Plant* and the *Efficiency of the Warren Mechanical Filter*. Both papers were published privately.

TABLES AND OTHER DATA.

TABLE I.

(From Professor Van Ermengem's Report.)

QUALITY OF OLD RHINE WATER AT OUDSHOORN AT EACH
STAGE OF ITS PURIFICATION.

	Directly from the river.	From the cistern.	After filtration.	After ozonization.
Residue on evaporation,	0.222	0.220	0.284	0.294
Chlorine,.....	0.035	0.046	0.049	0.049
Albuminoid Ammonia,.....	0.00027	0.00015	0.00009	0.00006
Free Ammonia,.....	0.00010	0.00010	0.0003	0
Nitrites,	0	0	0	0
Nitrates,	0.0006	0.0008	0.0014	0.0012
Permanganate,	0.024	0.016	0.010	0.005
Microbes per c.c.,.....	10,802	18,991	385	0
Color,	yellow	yellow	pale yellow	no color
Odor,.....	faint	faint	faint	faint
Taste,	?	?	?	?
Appearance,.....	turbid	turbid	turbid	clear

TABLE II.
(From Professor Van Eimengem's Report.)
EFFECT OF (ZONIZATION OF (FILTERED) OLD RHINE WATER AT OUDSHOORN.

Serial No.	Date.	Type of Sterilizer.	Kind of Water.	No. of colonies of Bac- teria per c.c. before ozon- ization.	Mn. K MnO ₄ before ozon- ization.	Mg. ozone per liter of air.	Length of contact.	Results, Samples sterile.	
								In all.	per ct.
I	29 XI 94	Experimental.	Filtered Water.	862	—	0.058	—	7 in 8	86.5
II	29 XI 94	"	Filt. Water and Bac- illus Fluorescens.	3,893	—	0.045	—	10 in 10	100.0
III	2 V 95	Improved.	Filtered Water.	4,080	0.32	0.042	4 min.	5 in 15	33.0
do	3 V 95	"	"	670	0.32	0.042	4 min.	7 in 12	58.3
do	4 V 95	"	"	258	0.35	0.045	4 min.	6 in 17	35.2
IV	7&18 V 95	"	"	1,270	0.40	0.039	7-8 min.	16 in 17	94.1
V	17 V 95	Large Apparatus.	"	"	—	—	—	—	—
VI	15 V 95	Experimental.	Filt. Water and B. Ramosus.	28,000	—	—	—	12 in 13	92.3
VII	15 V 95	"	Filt. Water, B. Sub- tilus and B. Rubi- ginosus.	32,000	—	—	—	17 in 18	94.4
VIII	15 V 95	Improved.	Filt. Water and B. Coli.	7,830,000	0.027	0.039	10 min.	12 in 12	100.0

TABLE III.

(From the Paper by Dr. Repin.)

QUALITY OF (FILTERED) SEINE WATER BEFORE AND
AFTER TREATMENT BY OZONE.

Results stated in parts per million.	Sample collected Sept. 18, 1896.		Sample collected Sept. 19, 1896.		Sample collected Sept. 20, 1896.	
	Before.	After.	Before.	After.	Before.	After.
Residue on Evaporation	242	240	241	242	256	248
Loss on Ignition,	24	20	24	24	28	24
Sulphate of Lime,	48.8	36.1	39.6	37.3	42.0	37.3
Carbonate of Lime,	103.6	107.8	128.9	127.1	112.5	101.8
Carbonate of Magnesia,	8.4	6.8	7.8	7.2	6.2	5.7
Chloride of Sodium,	41.0	41.0	29.3	29.3	29.3	29.3
Free Ammonia,	0.271	0.36	0.196	0.086	0.147	0.101
Albuminoid Ammonia,	0.364	0.202	0.536	0.198	0.287	0.205
Nitrous Acid,	0.0	0.0	0.0	0.0	0.0	0.0
Nitric Acid,	.142	.202	.71	.54	.274	.221
Phosphoric Acid,	0.0	0.0	0.0	0.0	0.0	0.0
Permanganate,	4.29	2.11	3.98	1.77	2.64	1.44

TABLE IV.

(From a Report by Professor Van Ermengem.)

EFFECT OF OZONIZING BRUSSEL'S WATER.

Before ozonization.	Collected Aug. 26, 1897.	Collected Sept. 2, 1897.	Collected Sept. 4, 1897.	Collected Sept. 6, 1897.
Colonies per c.c. after 8 days,	916	1056	1728	612
Organic matter,	0.035	0.043	0.038	0.039
Chlorine,	0.012	0.018	0.018	0.017
Color at a depth of 60 centimeters,	yellow, slightly opalescent.	id.	id.	id.
Taste,	good.	id.	id.	id.
Smell,	good.	id.	id.	id.
After ozonization.				
Colonies per c.c.,	14 samples give an average 20 colonies.	10 sterile samples. ¹	12 sterile samples. ²	10 sterile samples.
Organic matter,	0.022	0.028	0.028	0.016
Chlorine,	0.012	0.019	0.018	0.0175
Nitrites,	0	0	0	0
Color at a depth of 60 centimeters,	bluish, absolutely transparent.	id.	id.	id.
Taste,	good.	id.	id.	id.
Smell,	good.	id.	id.	id.
Conditions under which the experi- ments took place, ...	Discharge : 300 liters per min. Voltage : 85. Contact : 5 min. Concentration of ozone : 0.0025 to 0.003.	id. 110 id.	id. 90 to 100 id.	id. 90 to 100 id.
		0.0042	0.004	0.004

¹ One tube gave a single colony of *Bac. fluor. liq.* probably arising from the air.² Three tubes gave some colonies of the same microbe.

TABLE V.

(From a Report by Professor Van Ermengem.)

EFFECT OF OZONIZING WATER FROM OSTENDE, AND THE
CANALS OF PLASCHENDAEL AND BRUGES.

	Water from the Ostende Water Supply.	Purified Water from the 'st- ende Wat. Sup.	Water from the Canal at Plaschendael.	Water from the canal at Bruges.
Before Ozonization.	Collected Sept. 2, 1897.	Collected Sept. 2, 1897.	Collected Sept. 15, 1897.	Collected Sept. 15, 1897.
Colonies per c.c....	6,528	6,848	389,280	1,430,000
Organic Matter....	0.0985	0.0361	0.080	0.102
Chlorine.....	0.280	0.298	0.124	0.208
H ₃ N saline.....	mgr. 0.66	0.06	0.01	0.9
H ₃ N albuminoid...	mgr. 0.35	0.21	0.18	0.31
Nitrites.....	0	Trace.	Trace.	Trace.
Nitrates.....	Trace.	Trace.	Trace.	Trace.
Resid. on Evap.....	0.742	0.896	0.556	0.696
Loss by Calcin.....	0.80 blackened	0.108 blackened.	0.120	0.108
Color.....	yellowish, muddy.	id	yellowish.	dirty green, brownish
Taste.....	muddy	id	id	very dirty green
Smell.....	marshy	id	id	very dirty green
After Ozonization.				
Colonies per c.c....	10 sterile samples	10 sterile samples.	10 sterile samples.	10 sterile samples
Organic Matter....	0.0635	0.022	0.052	0.055
Chlorine.....	0.268	0.271	1.104	0.184
H ₃ N saline.....	0	0	0	0.1
H ₃ N albuminoid...	mgr. 0.01	0.06	0.04	0.18
Nitrites.....	0	0	0	0
Nitrates.....	Trace.	0	Trace.	Trace.
Resid. on Evap.....	0.728	0.610	0.475	0.736
Loss by Calcin.....	0.082	0.060	0.120	0.080
Color.....	null bluish	id	id	Slightly pinkish after having been greenish.
Taste.....	good	id	id	id
Smell.....	good	id	id	id
Conditions under which the ex- periments took place.	Discharge: 1.5 liters P. M. Voltage: 90. Contact: 5 min. Concentration of ozone: 0.004	id id id 0.004	2 liters. 100 6.8 min. 0.00374	2 liters. 100 6-8 min. 0.00374

TABLE VI.

(From Professor Leon Gerard's Report.)

DETAILS CONCERNING THE PRODUCTION OF OZONE BY THE
TINDAL SYSTEM AT THE BRUSSELS EXPOSITION.

Current supplied to Transformers.			Liters of air ozonized per minute.	Grams of ozone per hour.	Grams of ozone per cm. of air.	Total work consumed in Watts.	Watts per gram of ozone.
Amperes.	Volts.	Watts.					
22.6	73.64	1665.26	39.875	7.35	3.07	1858(H. P., 2.5)	252
28.55	80.50	2298.28	41	10.578	4.3	2568(H. P., 3.45)	244

CROTON WATER BEFORE AND AFTER TREATMENT BY OZONE.

Parts per million.		
	Before.	After.
Turbidity,	none	none
Color,	2½	1
Odor. { Cold,	none	none
	Hot,	none
Chlorine,	4.	4.
Residue on Evaporation,	54.	54.
Loss on Ignition,	33.	30.
Nitrogen as { Albuminoid Ammonia,	.170	.090
	Free Ammonia,	.060
	Nitrites,	trace
	Nitrates,	.800
Bacteria per c.c. after 48 hours in gelatin,	416	44

March 16, 1899.

QUALITY OF CROTON WATER BEFORE AND AFTER
OZONIZATION.

Date. 1899.	Period of Contact.	Permanganate.			Bacteria per c.c.			Color.		
		Before.	After.	Percent. Dif.	Before.	After.	Percent Dif.	Before.	After.	Percent. Dif.
Mar. 14.	10 min.	1.8	1.7	5.5	560.	320	42.8	1.50	1.00	30.00
" 21.	15	1.9	1.6	15.7	721	91	87.5	2.00	1.00	50.00
" 28.	20 min.	1.9	1.5	20.5	3,938	512	86.9	2.00	1.00	50.00
Apr. 7.	10	1.7	1.6	8.5	13,018	2,373	81.9	2.00	1.75	12.50

CROTON WATER BEFORE AND AFTER TREATMENT BY OZONE,
SHOWING THE EFFECT OF PROTRACTED OZONIZATION.

	Color.	Perman. of Pot.	Bacteria per c.c.	Minutes ozonated.
Croton water before treatment,.....	2½	1.90	483	0
Croton water after treatment,	1	1.65	216	10
Croton water after treatment,	1	1.50	143	20
Croton water after treatment,	1	1.50	120	30

March 29, 1899.

ESTIMATION OF THE YIELD OF OZONE.

Ozonized air and CO_2 are bubbled through a 5 % solution of KI. The I is thrown out of combination with K, which becomes caustic and takes up CO_2 . The iodine is titrated with freshly made solution of sodium hyposulphite.

KI is not decomposed by nitrites, nitrates or ammonia, but peroxide of hydrogen produces the same effect as ozone. Peroxide of hydrogen is probably not present in the ozonized air since the air before passing into the silent discharge is carefully dried, having no hydrogen to form in combination.

OZONE PRODUCED BY EXPERIMENTAL APPARATUS.

Experiment No.	Cubic feet air used.	Time con- sumed in minutes.	Rate of cubic ft. air in minute.	Mgs. oxygen converted into O_3 .	Mgs. ozone per cubic feet air.
1	0.5	15	30	36.95	73.90
2	0.5	15	30	35.9	71.80
3	0.3	5	16	16.0	53.30
4	0.1	4	40	8.625	86.25
5	0.1	2	20	5.95	59.50
ozonizer short circuits.					
6	0.1	4	40	9.5	95.0
7	0.2	7	35	16.6	83.0

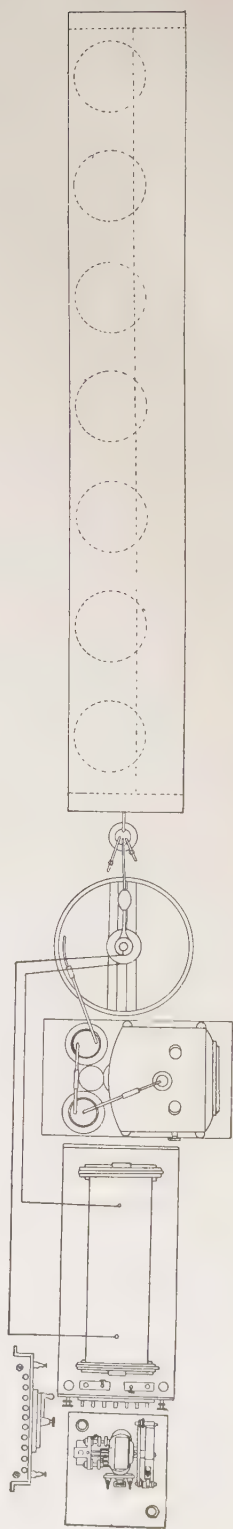
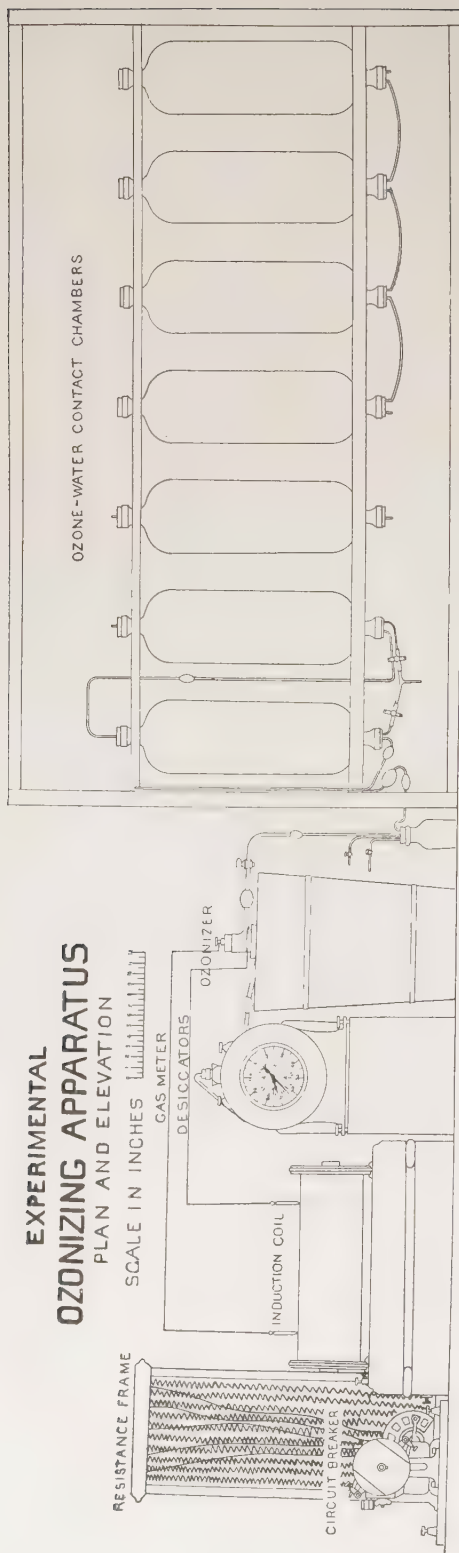
Excluding the results of experiment No. 3 as being inaccurate from the excessive speed with which the air was bubbled through the KI solution, and No. 5, for the reason that the ozonizer was short-circuited, we have, for the average results of the estimations:

No. 1,	73.9	mgs. ozone	per cu. ft.	at rate of 1 cu. ft. air in	30 min.
2,	71.8	"	"	" "	30
4,	86.2	"	"	" "	40
6,	95.0	"	"	" "	40
7,	83.0	"	"	" "	35
5)409.9					5)205

Average, 81.98 mgs. ozone per cu. ft. air at the rate of 1 cu. ft. air in 41 min.

MARCH 29, 1898.

EXPERIMENTAL OZONIZING APPARATUS PLAN AND ELEVATION SCALE IN INCHES



SKETCH OF OZONIZER

SCALE
0 1 2 3 4 5 6
INCHES

